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Magneto-electric response in $(1-x)\text{PbZr}_{0.65}\text{Ti}_{0.35}\text{O}_3-x\text{BaFe}_{12}\text{O}_{19}$ multiferroic ceramic composites

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The magneto-electric (ME) properties of $\text{PbZr}_{0.65}\text{Ti}_{0.35}\text{O}_3\text{--BaFe}_{12}\text{O}_{19}$ (PZT–BaM) multiferroic ceramic composites have been investigated in this work. These materials, containing both the ferroelectric PZT and ferrimagnetic BaM phases, were prepared from the conventional solid-state reaction method, and their main (micro)structural characteristics are provided. The ME measurements were performed over wide frequency and temperature ranges, and the influence of the BaM content was appraised. An enhanced ME coefficient (α) was obtained for the applied magnetic field of 0.8 kOe, at 97 kHz. In addition, the results reveal a high thermal stability of α in the whole analyzed temperature range, showing that the studied PZT-based ceramic composites have great potential for practical applications.

Keywords: multiferroics; ceramic composites; PZT; $\text{BaFe}_{12}\text{O}_{19}$

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I. Introduction

Since the last decade, there has been an increasing interest in the investigation of the physical properties of multiferroic materials, because of their remarkable technological potential for applications in novel multifunctional devices.¹ In fact, the synthesis and development of multiferroic systems, which simultaneously exhibit two or more of the fundamental ferroic orders, ferroelectric, ferro/ferrimagnetic and/or ferroelastic, have been intensified in the recent years from both scientific and technological points of view.² Specially, the coupling between the electric and magnetic order parameters, the so-called magneto-electric (ME) effect,³ gives rise to novel physical phenomena, which make them promising materials for potential applications in spintronics and communication industry.^{2,4}

In this topic, works in the literature have considered investigating the physical properties of multiferroic systems including both single phases (which simultaneously show high magnetization and polarization)^{5,6} as well as multi-phase composites,^{7,8} where individual ferroelectric and ferro/ferrimagnetic phases, with enhanced piezoelectric and magnetostrictive properties, respectively, are present. In all these cases, many efforts have been dedicated to improve the ME response by achieving a better connectivity and coupling of the strains generated in the constitutive phases under the influence of applied external fields.

The present work concerns an investigation of the physical properties of multiferroic composites based on ferroelectric $\text{PbZr}_{1-y}\text{Ti}_y\text{O}_3$ (PZT) and ferrimagnetic $\text{BaFe}_{12}\text{O}_{19}$ (BaM) systems, showing individually excellent piezoelectric and magnetostrictive responses, respectively. In spite of this fact, the current literature registers only few works on these composites, on which some studies on dielectric,⁹ conduction,¹⁰ as well as multiferroic properties can be found,^{11,12} but with no evidence of a detailed investigation on their ME response. Two such approaches merit to be here mentioned. First, Srinivasan *et al.* recently reported some evidences of ME response in bilayers compounds based on single crystal BaM and polycrystalline PZT, by millimeter-wave magneto-

electric interactions through the effect of the electric field on magnetic excitations.¹¹ A mechanical deformation (or strain) produced by the applied electric field promotes a shift in the frequency of the electromagnetic modes in the magnetic component, resulting in a relatively small ME signal response.¹³ Second, Guerra *et al.* have also recently reported, for the first time, real evidences of the ME coupling in PZT–BaM multiferroic composites.¹² In this case, the interaction between the electric and magnetic ferroic components was confirmed through measurements of the magneto-dielectric (MD) effect, revealing improved MD coefficient, when compared to the reported values for other single-phase and particulate multiferroic composites.^{14,15} Nevertheless, evidence of large ME coupling has not yet been reported for this system.

In this work, the magneto-electric (ME) coupling has been investigated in (1-*x*)PbZr_{0.65}Ti_{0.35}O₃–*x*BaFe₁₂O₁₉ (PZT–*x*BaM) multiferroic ceramic composites, prepared from the conventional sintering method. The ME response was obtained by measuring the ME voltage (or ME coefficient) from the samples, when subjected to simultaneously applied DC and AC magnetic fields. The results reveal enhanced ME coefficient, which shows to be strongly dependent on the BaM content. Moreover, the high thermal stability of this ME response, as we observed over a wide temperature range, makes this composite system promissory for practical applications, in which an enhanced and thermally-stable ME response is required.

II. Experimental Procedure

PZT–*x*BaM ceramic composites based on PbZr_{0.65}Ti_{0.35}O₃ (PZT) and BaFe₁₂O₁₉ (BaM) ferroelectric and ferrimagnetic phases, respectively, were obtained from the solid-state reaction method. For the PZT phase, precursor PbO (99 % pure, Sigma-Aldrich/VETEC, São Paulo, Brazil), ZrO₂ (99.99 % pure, Riedel-de Haën, Seelze, Germany) and TiO₂ (99 % pure, LAFAN Química Fina Ltda, São Paulo, Brazil) powders were mixed in the appropriate proportions, ball-milled for 8 h and then calcined at 950 °C for 2.5 h. For the BaM phase, the precursor powders were BaCO₃ (99 % pure,

Sigma-Aldrich/VETEC, São Paulo, Brazil) and Fe_2O_3 (99 % pure, Sigma-Aldrich/VETEC, São Paulo, Brazil), also mixed in the appropriate amounts, followed by ball-milling for 8 h and calcination at 1000 °C for 3.5 h. Subsequently, the composites were prepared by mixing the PZT and BaM phases according to the nominal relation $\text{PZT}_{(1-x)}\text{BaM}_x$, where $x = 0.03, 0.04$ and 0.05 . After a milling process, the powders were uniaxially cold-pressed in disc-shaped samples by using a 10 MPa pressure, and then sintered in closed alumina crucibles at 1250 °C for 3 h. Ceramic samples with finally 5 mm in diameter and about 1 mm in thickness were obtained. The samples are hereafter labeled as BaM100x, i.e., BaM003, BaM004 and BaM005, representing nominally 13, 17 and 20 % BaM volume fraction in PZT, respectively. The structural characteristics of the composites were investigated from x-ray diffraction (XRD) technique by using a Shimadzu XRD 6000 (Tokyo, Japan) diffractometer with Cu K_α radiation. The XRD data were analyzed by Rietveld refinement using the Fullprof Suite Package.¹⁶ Silver electrodes were applied on the two opposite surfaces of the sample by a thermal treatment at 590 °C, in order to obtain the electric properties. The converse piezoelectric response was studied at room temperature and frequencies of 200, 400 and 800 mHz, by using a system comprising an HP33120A Arbitrary Waveform Generator (Santa Clara, CA), a Trek Model 662 Amplifier (Medina, NY) and a Solartron LVDT AX/0.5/S Displacement Transducer (West Sussex, United Kingdom). The magnetic response was obtained at room temperature by using a SQUID Vibrating Sample Magnetometer (Quantum Design MPMS-5S, San Diego, CA). The magneto-electric response was investigated by using a static DC Electromagnet, powered by a bi-polar power supply allowing application of a static (DC) magnetic field on the sample. Low powered Helmholtz coils were used to produce an AC field that was superimposed with the strong DC magnetic field. The ME voltage response was then measured in a wide frequency range (0–100 kHz) through a SR850 digital lock-in amplifier (Sunnyvale, CA), from cryogenic temperatures (100 K) up to 325 K. The samples were poled under a DC electric

field of 20 kV/cm at 80 °C for 30 min, and cooled to room temperature before carrying out the ME measurements.

III. Results and Discussion

Figure 1 shows the x-ray diffraction patterns and Rietveld refinement results obtained on the powdered ceramics for all the studied composites. The pseudo-Voigt functions were used to fit the peak profile of both PZT and BaM phases based on $R3c$ (rhombohedral symmetry) and $P6_3/mmc$ (hexagonal symmetry) spaces groups, respectively. The experimental data are presented by open symbols (o) and the theoretical data are shown as solid lines. The difference between experimental and theoretical data is shown as bottom lines, while the cross symbols as well as the vertical lines represent the allowed Bragg's peaks for the PZT and BaM phases, respectively. Both ferroelectric rhombohedral ($R3c$) PZT and ferrimagnetic hexagonal ($P6_3/mmc$) BaM structures were confirmed in all the studied cases. No trace of secondary phases was detectable. The refinement parameters, R_F and R_B refinement reliability factors, obtained based on structure factors and pattern intensities, for both $R3c$ and $P6_3/mmc$ phases, as well as the unit-cell volumes for the $R3c$ phase (V_R), are shown in Table I. As can be seen, the unit cell volume for the PZT phase in these composites reveals a slight decrease with the increase of the BaM content.

For analyzing the result just above, the following observation applies. As we reported elsewhere,⁹ the values of ferroelectric-paraelectric transition temperature (T_C) at 100 kHz in these materials show some variation, that is, about 301, 274 and 257 °C for BaM003, BaM004 and BaM005, respectively. From both the oxidation state and ionic radii (IR) mismatch viewpoints, proposing incorporation of some Ba^{2+} cations into PZT appears to be reasonable, but in an apparently modest amount, that is, considering the excellent XRD data refinement obtained even when ignoring, during peak profile fitting, this reaction-derived solid solution development. In any case, partial substitution of Pb^{2+} by Ba^{2+} would be expected to induce a decrease in the T_C value as

well as an increase in PZT cell volume considering that $IR(Ba^{2+}) > IR(Pb^{2+})$,¹⁷ contrasting with the trend concluded from our XRD results (Table I), a trend of which suggests the PZT crystal lattice to be facing a straining in these composites in the presence of the BaM ferrimagnetic phase. This is similar to the result observed, for instance, in ferroelectric $Pb_{0.93}La_{0.07}(Zr_{0.60}Ti_{0.40})O_3$ (PLZT) and ferrite $NiFe_2O_4$ (NFO) composites,¹⁸ showing a decrease in PLZT tetragonality (c/a) with increasing ferrite. Both the above small doping and straining effects should have an influence on the microstructural characteristics of these PZT- x BaM composites, whose scanning electron microscopy images from polished surfaces (not shown here) reveal a decrease in average grain size, the values estimated being 3.17, 3.0 and 2.73 μm for BaM003, BaM04 and BaM005, respectively.¹⁹

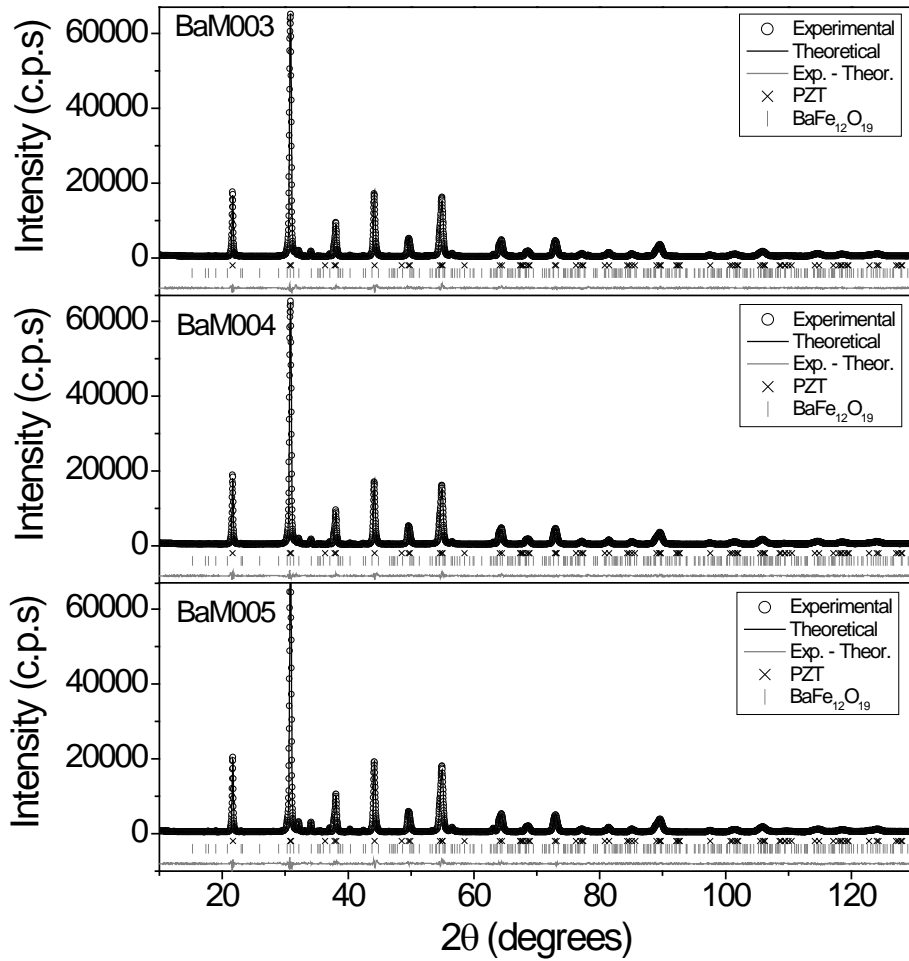


Fig. 1. X-ray diffraction patterns and Rietveld refinement results of the studied composites, obtained at room temperature.

Table I. Reliability factors (R_F and R_B) and the unit-cell volume (V_R) for the PZT phase obtained from the refinement processes, for the BaM003, BaM004 and BaM005 composites.

Sample	R _F (%)	R _B (%)	R _F (%)	R _B (%)	V _R (Å ³)
	PZT		BaM		
BaM003	0.9	1.4	1.9	4.8	136.211
BaM004	0.8	1.0	2.2	3.3	136.206
BaM005	1.1	1.8	2.3	3.4	136.188

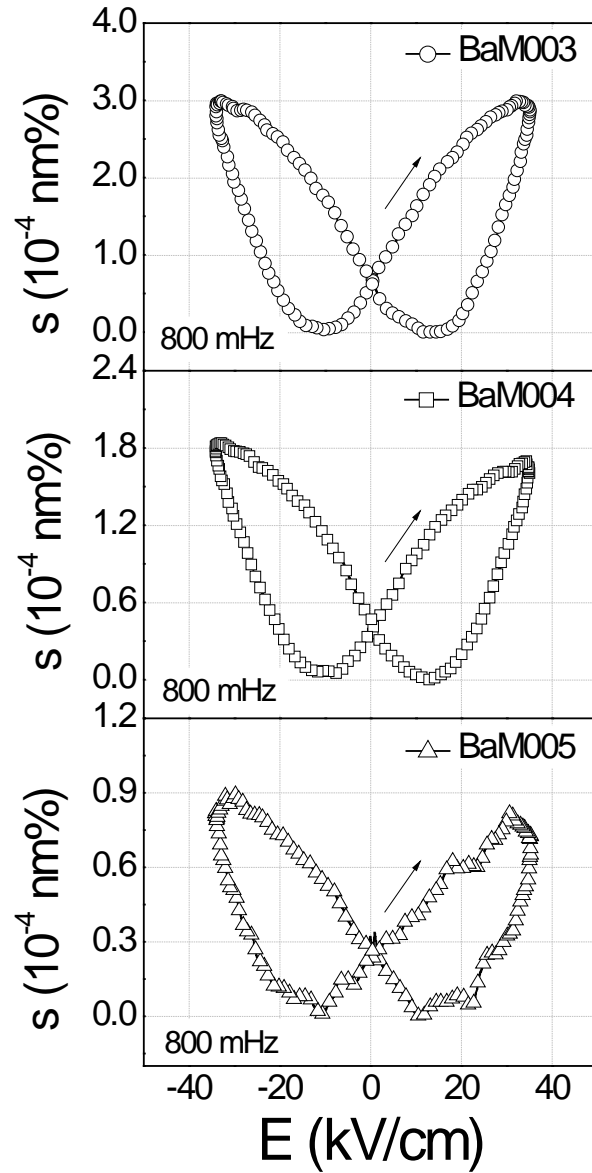


Fig. 2. Electric field dependence of the strain (s - E butterfly hysteresis loop) for the studied BaM003, BaM004 and BaM005 composites, as recorded at room temperature.

In ferroelectric materials, besides a measurable polarization–electric field hysteresis loop (P - E loop), the polarization switching produced by an applied electric field is expected to also lead to a strain–electric field hysteretic behavior (s - E loop, or converse piezoelectric response). The electric field dependence of the strain (s) for BaM003, BaM004 and BaM005 is illustratively shown in Fig. 2 for the frequency of 800 mHz. As can be noticed, the data reproduce well butterfly-like hysteresis loops in all these cases, as a result of the piezoelectric activity in these composites. This behavior can be associated to the switching and motion of the ferroelectric domain walls. Results for 200 and 400 mHz were qualitatively similar, but with a slightly higher data distortion related to conduction processes, as also expected for higher BaM content, which is the case of BaM005 in this Fig. 2. Development of conduction processes, coming from the BaM magnetic phase and ascribed to super-exchange (of $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$ type) as well as double exchange (of $\text{Fe}^{3+}\text{--Fe}^{2+}$ type) interactions in ferrite systems has been discussed in a previous work, the analysis of which included applying the Jonscher’s universal relaxation law.¹⁰

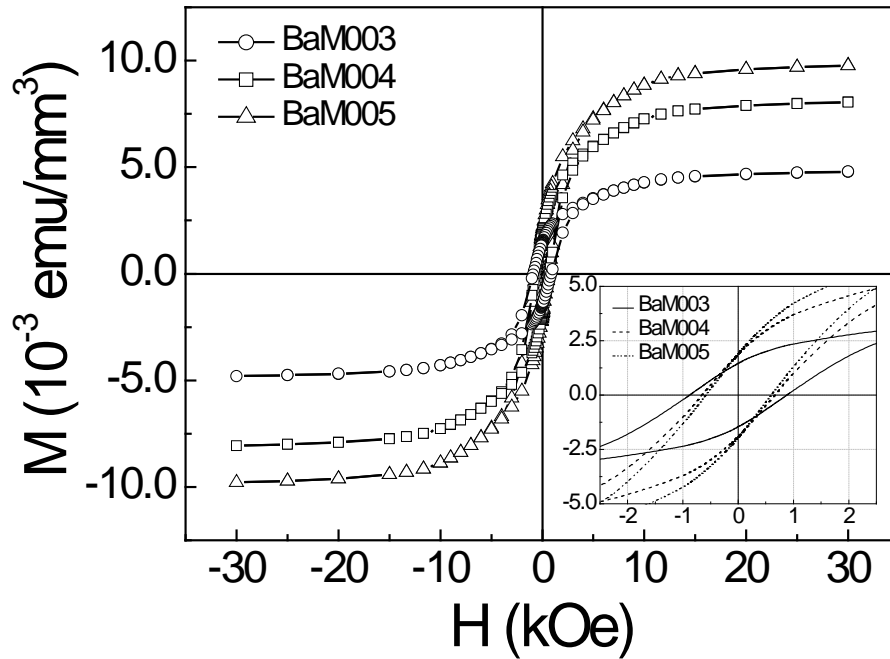


Fig. 3. Magnetic field (H) dependence of the magnetization (M) measured on the BaM003, BaM004 and BaM005 composites at room temperature. The inset shows the enlarged central part of the M - H curves.

Figure 3 shows the magnetic field dependence of the magnetization (M - H hysteresis loop) of these BaM003, BaM004 and BaM005 composites, as measured at room temperature. The figure inset is a magnification of these M - H curves toward the central region. Typical ferromagnetic hystereses with saturation magnetization when approaching 25 kOe are observed in all these cases. Table II shows the values obtained for the remnant magnetization (M_R) and the coercive field (H_C) for these composites. M_R increases gradually with increasing the BaM content, whereas H_C decreases. The remnant magnetization values are comparable to those values obtained in typical ferromagnetic materials,²⁰ but are higher than those obtained for other single phase²¹ and composite-like multiferroic systems.^{22,23}

Table II. Remnant magnetization (M_R) and coercive field (H_C), obtained from the M - H curves of Fig. 3, and direct piezoelectric coefficient (d_{33}) values, for the BaM003, BaM004 and BaM005 composites.

Sample	M_R (10^{-3} emu/mm ³)	H_C (kOe)	d_{33} (pC/N)
BaM003	1.46	0.90	95
BaM004	1.91	0.69	51
BaM005	1.92	0.59	39

In a previous work by the present authors, evidence of a coupling between the electric and magnetic components in the PZT- x BaM composite with $x = 0.03$ was presented.¹² In that case, the interaction between the involved ferroic phases was investigated by measuring the effect of an external DC magnetic field on the dielectric response of the samples, well known as magneto-dielectric (MD) effect. Results revealed a high MD coefficient (close to 6 %) and low dielectric losses at 0.6 kHz, under an applied DC magnetic field of 2 kOe, which represent enhanced properties when compared to other typical multiferroic systems.^{14,15} In passing, the MD response

we have been measuring for the BaM004 and BaM005 composites, at 2 kOe and 0.6 kHz, reveals maximum MD coefficients as low as 0.91 % and 0.16 %, respectively.

To complete our study, we have chosen in this work to also investigate the magneto-electric (ME) response from these composites, by measuring the ME voltage (or ME coefficient) on the samples, when subjected to simultaneously applied DC and AC magnetic fields. Just recalling that before performing these measurements, the samples were first poled in a DC electric field (20 kV/cm at 80 °C) for ME coupling enhancement. In passing, the piezoelectric coefficient values (d_{33}) of the samples were obtained from the direct piezoelectric effect by using a KCF Technologies PM3500 d_{33} Meter. The measured values, which are also shown in Table II, are about 95, 51 and 39 pC/N for BaM003, BaM004 and BaM005, respectively. We believe that both small doping and straining effects in the PZT phase, as discussed above, should likely be influencing these values.

Back to the ME response, Fig. 4 depicts the frequency dependence of the coefficient (α) measured for the BaM003 composite, at room temperature and different applied DC magnetic fields, the results of which were similar for the other composites, qualitatively speaking. For a quantitative comparison, Fig. 5 shows the frequency dependence of the ME coefficient data from the three studied composites, at the DC magnetic field of 0.8 kOe where these α values appeared to be intensified. What is seen in these figures is that the ME coefficient continuously increases with increasing frequency, reaching its maximum value around 97 kHz for all these composites, and then decreases for a further increase in frequency. This behavior is likely related to the interactions of the ferroic components being significantly improved at the electromechanical resonance frequency from either the radial or the thickness acoustic modes.^{24–26} This approach is based on the fact that the ME coupling in magnetostrictive/piezoelectric composites is known to be usually mediated by the mechanical strain. Therefore, a significant increase of the ME coefficient is to be expected around the resonance frequencies, which scale in the kHz range for conventional sample dimensions

and radial acoustic modes, as has also been suggested elsewhere for some typical magneto-electric systems, where the maximum value of α was found to occur at 100 kHz.²⁴

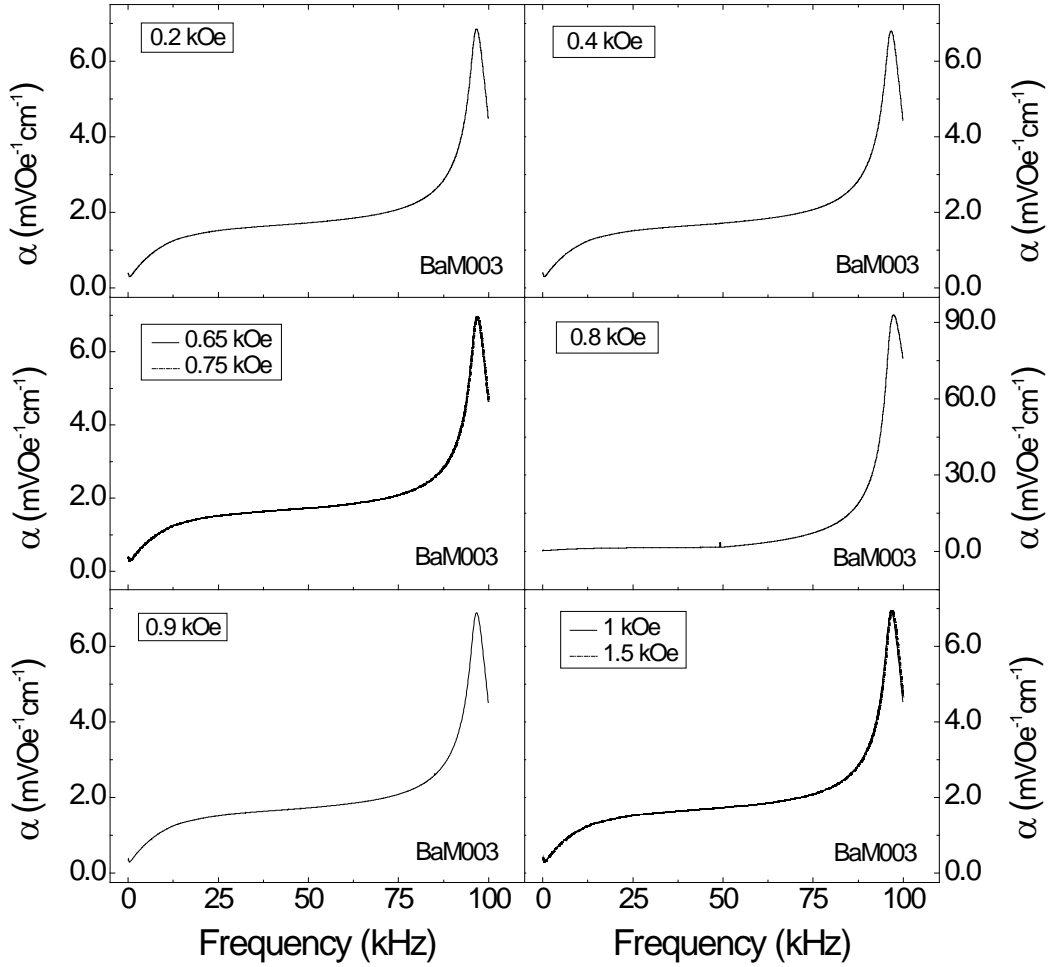


Fig. 4. Frequency dependence of the magneto-electrics (ME) coefficient (α), for the BaM003 composition, at room temperature and different applied DC magnetic fields, as an illustration for the behavior pattern found for all the studied samples.

The dependence of the maximum ME coefficient (found at 97 kHz) on composition is given in the inset of Fig. 5 (data corresponding to 0.8 kOe). A linear-like decrease of the α coefficient is observed with increasing the BaM content, the values being 94.7, 70.9 and 48.3 mV/Oe⁻¹cm⁻¹ for the BaM003, BaM004 and BaM005, respectively. To approach this result, one should remember that by applying a magnetic field, a strain is induced in the magnetic phase (magnetostrictive effect). The magnetic field-mediated strain will subsequently induce a stress in the piezoelectric component,

resulting in a measurable electric field (or voltage) which promotes domains orientation in the ferroelectric phase and, thereby, appearance of a net polarization in the sample. Accordingly, the decreasing behavior of the ME coefficient when the BaM content is increased could likely be associated to the strength of the magnetostrictive response from the magnetic phase in such composites.^{27,28} Therefore, we chose to evaluate the magnetostrictive component influencing the ME response, the magnetostriction coefficient (λ) being appraised from the samples' surface displacement for, representatively, the BaM003 and BaM005 composites. The measurements were conducted by using an UHF-120 Polytec Vibrometer (Irvine, CA), working on Laser Doppler Effect, conjugated with a WavePro 725Zi Lecroy Oscilloscope (Chestnut Ridge, NY). The applied DC and AC magnetic fields were 100 Oe and 2 Oe, respectively, covering a broad frequency range using a SMBV100A Rohde & Schwarz–Vector Signal Generator (München, Germany). The obtained maximum values for the effective magnetostriction coefficient were around 70 and 55 ppm for BaM003 and BaM005, respectively. This result is in line with observation of a higher ME response for the BaM003 sample. Further studies are currently in progress to advance discussion on this topic of sources of direct or indirect magneto-electric modulation in such multiferroic composites. In any case, just to mention that the α value found here for the BaM003 composite ($94.7 \text{ mVOe}^{-1} \text{ cm}^{-1}$) seems to be much higher than the values reported for some typical multiferroic composites.^{29,30}

Figure 6 shows the temperature dependence of the ME coefficient for these BaM003, BaM004 and BaM005 composites, at the fixed applied DC magnetic field of 0.8 kOe and frequency of 97 kHz. As can be seen, a high stability of α was observed for all the samples, in the entire analyzed temperature region. From the technological point of view, magneto-electric systems-based sensor devices, optimized for use in practical applications, are often limited to operate under special conditions because of their temperature dependent response;^{31,32} this is because, as observed in many cases, the polarization as well as DC resistances are highly temperature dependent

parameters. Such changes may potentially affect the performance of ME-based devices depending on the temperature region where the materials in concern are being or going to be used. Therefore, the present results suggest that the PZT–BaM based multiferroic system has great potential for practical applications, by using its enhanced ME response toward a wide temperature range. For reference, we note that the Neel's temperature for pure BaM locates around 460 °C,³³ meaning that the present work has been conducted toward the ferrimagnetic region to be nominally expected in these composites.

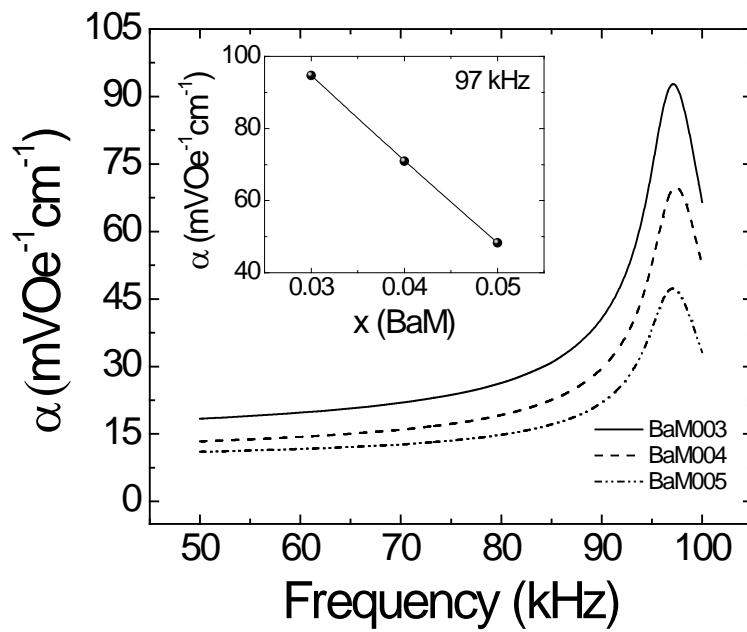


Fig. 5. Frequency dependence of the magneto-electric (ME) coefficient (α), for the BaM003, BaM004 and BaM005 composites, at room temperature and a magnetic field of 0.8 kOe. The inset shows the maximum values of the coefficient obtained at 97 kHz for all these samples.

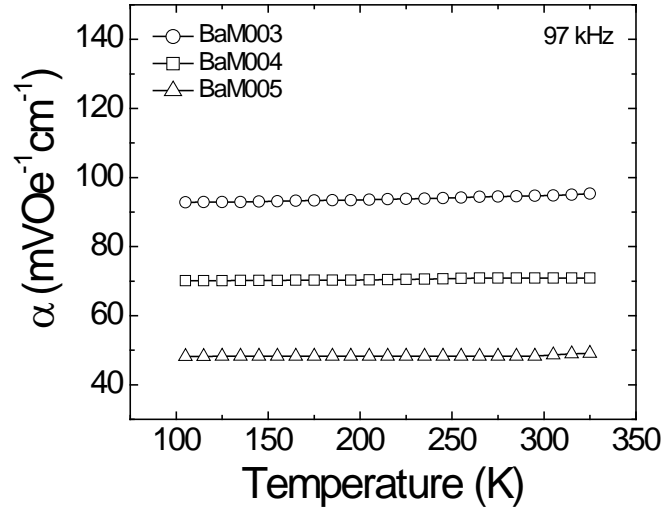


Fig. 6. Temperature dependence of the magneto-electric (ME) coefficient (α) for the BaM003, BaM004 and BaM005 composites, at 0.8 kOe and 97 kHz.

IV. Conclusions

The magneto-electric properties of PZT–BaM based multiferroic composites, synthesized by conventional sintering, have been investigated. The frequency dependence of the ME coefficient revealed a maximum peak around 97 kHz for the BaM003, BaM004 and BaM005 composites studied here. This result appears to arise from multiferroic interactions improvement at the electromechanical resonance frequency related to the radial acoustic modes. Enhanced ME coupling was observed for the BaM003 composition and the value obtained for the ME coefficient approaches the highest values so far reported for some typical multiferroic composites. The high stability of the ME response with the temperature suggests that PZT–BaM based multiferroic composites could be potential candidates for electronic device applications.

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